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Frequency- and Power-Dependent Photoresponse of a Perovskite Photodetector Down to the Single-Photon Level

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ABSTRACT: Organometallic halide perovskites attract strong interests for their high photoresponsivity and solar cell efficiency. However, there was no systematic study of their power- and frequency-dependent photoresponse types in methylammonium lead iodide perovskite (MAPbI₃) photodetectors. In the first type, the photoresponse remains constant from 5 Hz to 800 MHz. In the second type, absorption of a single photon can generate a persistent photoconductivity of 30 pA under an applied electric field of 2.5×10^4 V/ cm. Additional absorbed photons, up to 8, linearly increase the persistent photoconductivity, which saturates with the absorption of more than 10 photons. This is different than single-photon avalanche detectors (SPADs) because the single-photon response is persistent as



long as the device is under bias, providing unique opportunities for novel electronic and photonic devices such as analogue memories for neuromorphic computing. We propose an avalanche-like process for iodine ions and estimate that absorption of a single 0.38 aJ photon triggers the motion of 10^{8-9} ions, resulting in accumulations of ions and charged vacancies at the MAPbI₃/electrode interfaces to cause the band bending and change of electric material properties. We have made the first observation that single-digit photon absorption can alter the macroscopic electric and optoelectronic properties of a perovskite thin film.

KEYWORDS: Perovskite, photodetectors, single-photon sensitivity, ion migration, impact ionization

rganometallic halide perovskites have demonstrated extraordinary optical-electrical conversion efficiency as photovoltaic devices and enormous responsivity as photodetectors.¹⁻¹¹ One general observation among all perovskite detectors is that its photoresponsivity is sensitive to the input light intensity. As the light intensity increases, the responsivity decreases. However, to our best knowledge, there have been no systematic studies about power- and frequency-dependent responsivity for perovskite detectors. Several groups have reported the high-frequency response without specifying the power level and the corresponding responsivity at high frequency¹²⁻¹⁴. Other groups reported power-dependent responsivity under DC measurements, without considering the frequency dependence of responsivity.^{15,16} We believe a comprehensive study of the photoresponsivity of perovskite devices under different frequencies and optical power levels is important not only from an application point of view but also for understanding the physics of the optical process in organometallic halide perovskites. In this work, we probed solution-processed polycrystalline methylammonium lead iodide (MAPbI₃) to investigate its power- and frequencydependent photoresponse. By doing so, we observed several interesting characteristics that shed light on the intrinsic physical mechanisms of perovskite detectors and new opportunities for applications.

We found that over the frequency range from 5 Hz to 800 MHz, the device photoresponsivity decreases with the input optical power following the relation $R \propto P^{-\alpha}$ with $\alpha \sim 0.4$ and P being the input light power. This relation holds over a wide frequency range of more than 8 orders of magnitude. Over this frequency range, the temporal response of the detector follows the waveform of the modulating light intensity. However, as we investigated the extremely low-frequency response (near DC), we found that the perovskite detectors display the characteristics of persistent photoconductivity with a very slow response. In this regime, the power-dependent photorespon-

Received: January 13, 2020 Published: February 6, 2020 sivity mostly follows the relation $R \propto P^{-\beta}$ with $\beta \sim 0.9$. Most strikingly, we found that in the low-frequency or persistent photoresponsivity regime, the device can respond to single photons. Our detailed study shows that, in the extremely low light intensity regime, where less than 10 photons are absorbed by the device, the photoresponse is actually proportional to the input photon number (i.e., $R \propto N$ with N being the number of photons absorbed by the perovskite material). However, as the photon number increases, the photoresponse enters the regime of $R \propto P^{-\beta}$ with $\beta \sim 0.9$. In this work, we report the detailed measurement results in different frequencies and power levels down to single-digit photons. We also propose possible mechanisms causing such unique characteristics for perovskite devices.

Experimental Setup and Methods. The testing device has a vertical structure consisting of indium tin oxide (ITO; 180 nm thickness)/perovskite (400 nm)/ITO (110 nm) (Figure 1a), with an active area of 7 μ m in diameter. Device



Figure 1. Device layout and dark IV. (a) Schematic diagram of a device structure with the material and thickness of each layer (3D and top view). (b) Dark IV characteristics and the micrograph of a probed device.

dark IV characteristics, as well as the top view of a probed device, are shown in Figure 1b. The detailed fabrication process is illustrated in Figure 2.

For the solution preparation, we dissolved poly-TPD (40 mg) in 2 mL of chlorobenzene (CB) in a N₂ glovebox to get the 20 mg/mL solution. CH₃NH₃PbI₃ was prepared by mixing CH₃NH₃I (795 mg) and PbI₂ (2.3 g, 1:1 molar ratio) into DMF (2648 μ L) and DMSO (323 μ L) mixed solvents. All solutions were magnetically stirred at 60 °C and 1200 rpm for more than 12 h.

An ITO-deposited glass substrate was sonically cleaned in acetone, methanol, IPA, and deionized water (DI water) sequentially and then blown dry with N₂. After the solvent cleaning, the ITO substrate was dipped in saturated KOH containing IPA solution for 1 h, then rinsed with IPA and DI water, and blown dry with N₂. Before the spin-coating of photoresist, the ITO substrate was baked at 120 °C for 30 min to remove adsorbed moisture at the film surface and then cooled to room temperature. For all of the photolithography steps, we spin-coated the negative photoresist layer thickness of around 1.5 μ m. All photolithography exposure steps were

performed by a laser writer (Heidelberg MLA150). After the photoresist patterning, we sputtered Cr (20 nm)/Au (100 nm) and lifted off the film in acetone. Cr/Au patterns were also formed as alignment markers for subsequent photolithography steps (Figure 2a).

We carried out another photolithography step (Figure 2b) to pattern the bottom ITO layer by wet-etching with 50% HCl (Figure 2c). Right before poly-TPD spin-coating, the patterned ITO substrate was baked at 120 °C for 30 min and then cooled down to room temperature. The 20 mg/mL poly-TPD solution was spin-coated with 600 rpm for 45 s, followed by 150 °C post bake for 30 min (Figure 2d). Using the patterned NR9-1500 as the mask (Figure 2e), we performed the O2 plasma etch of the poly-TPD layer. The photoresist was removed with acetone. The wafer was rinsed with DI water and blown dry with N_2 (Figure 2f). The perovskite solution was spin-coated onto the patterned substrate with 3500 rpm for 40 s. At the 10th second during spin-coating, 1 mL of ether was sprayed on the substrate. Then the sample was baked at 70 $^{\circ}C$ for 15 min (Figure 2g). The resultant perovskite layer is around 400 nm thick. A layer of 180 nm ITO was then sputtered onto the samples (Figure 2h). After overnight lift-off in chlorobenzene (CB) (Figure 2i), the sample was rinsed with CB and then blown dry with N₂. The last step, chlorobenzene (CB) lift-off, is critical to the overall device yield and performance. Unlike the conventional photoresist lift-off process in acetone, to facilitate the CB lift-off process, we have created a smooth contour for the top ITO electrode (Figure 1a) and a larger contact pad (100 μ m diameter). Regarding the asymmetric dark IV in Figure 1b, it is likely that the bottom ITO layer from a commercial ITO-on-glass substrate has slightly different properties than the sputtered top ITO layer formed in our laboratory. Depending on the method of deposition and deposition condition, the work function of the ITO layer can vary, causing asymmetric I-V characteristics.

In the optical setup for photoresponse characterization, the two beam splitter system couples both the input laser light and the illuminating light source onto the device under test (DUT), allowing us to visualize the device position as well as the beam spot through a CCD camera. Before the first beam splitter, there is a lens to focus on the input laser beam spot. A neutral density filter is placed in front of the focusing lens to attenuate the light power.

To avoid stray light, the perovskite photodetector device was put in a dark box. The device was electrically contacted with a ground-signal-ground (GSG) probe, with the output terminal connected to a Keysight B2902A precision source meter for slow-response measurement and IV characterization. The optical input was from single-mode fiber-pigtailed laser diodes of different wavelengths, driven by a Thorlabs CLD1010 compact laser diode controller.

For frequency-dependent characterization, the device was biased at 1 V and contacted with a GSG probe. In the frequency range from 5 Hz to 10k Hz, the photocurrent was measured by a lock-in amplifier, SR865A, following a low-noise current preamplifier, SR570. In the frequency range from 500 kHz to 800 MHz, the input light was modulated by Agilent N5182A, and the output photocurrent was measured by an HP 89410A vector signal analyzer with the preamplifier on. In the impulse response characterization, the device is biased at 1 V via a bias-T, and the output signal is amplified by a 1.5 GHz bandwidth MITEQ_AM-1300 low-noise amplifier (27 dB



Figure 2. Fabrication process. (a) Cleaned ITO glass substrate with Cr/Au alignment markers. Cr/Au alignment markers are in the center and four corners of a substrate, not shown in the device region. (b) Photolithography for wet etch mask. (c) Wet-etching of ITO. (d) Spin-coating of poly-TPD. (e) Photolithography for the dry etch mask. (f) Dry-etching of poly-TPD. (g) Spin-coating of perovskite and post bake. (h) ITO sputtering. (i) Lift-off in CB.



Figure 3. High-frequency characteristics at a 639 nm. (a) Frequency response from 5 Hz to 800 MHz. (b) Impulse response to a 5 ns square pulse (~50 μ W).

voltage gain and 1.4 dB noise figure) and measured by a digital oscilloscope (Agilent DSO80604B Infiniium High-Performance Oscilloscope).

In slow-response characterization, the laser was modulated by an Agilent 33600A series waveform generator to generate a series of 200 ms rectangular pulses in a manner described below. To record the device response to a single 200 ms optical pulse at a given power level, we programmed a LabVIEW file to control the device bias and optical pulses. At first, the bias on the device was ramped from 0 to 1 V at a rate of 0.2 V s⁻¹. After reaching 1 V bias, the waveform generator sent a single 200 ms laser pulse at the 10th second (i.e., 5 s after the device was biased at 1 V and the dark current became stable), and the program started to collect the data for timedependent photocurrent, which is the total current subtracted by the dark current, because it was observed that the photocurrent response to a single optical pulse rose with a time constant of the order of 10 s (0.1 Hz) until a constant current level was reached. Then the current output remains at the level in a manner of persistent photocurrent. Then the

LabVIEW program reset the device by reducing its bias voltage to 0 V, causing the current level to drop to zero in less than 140 s. After resting the device at zero bias for 3 min, the bias was ramped to 1 V again following the same cycle as before. In this manner, a series of perovskite detector responses to a single optical pulse at a given optical power level was measured.

We used four different structures, ITO/glass (substrate), ITO/ITO/glass, perovskite/ITO/glass, and ITO/perovskite/ ITO/glass, to carefully calibrate the amount of light absorbed by the perovskite layer. We used a Filmetrics profilometer to measure reflectivity and the percentage of transmitted light at different wavelengths. The fraction of light absorption by the perovskite layer in the ITO/perovskite/ITO/glass structure was characterized to be 0.75 at a 518 nm wavelength and 0.68 at a 639 nm wavelength. From the percentage of light adsorption, γ , by the perovskite layer, the optical power, $P_{\rm ph,PV}$, and the number of photons, $N_{\rm ph,PV}$, absorbed by the perovskite layer within the optical pulse width can be calculated by



Figure 4. Power-dependent response (639 nm). (a) Perovskite device power-dependent photoresponse under 10 Hz, 0.5 MHz, 5 MHz, and 51 MHz. The slopes are all close to -0.4. (b) Power-dependent slow (quasi-persistent) photoresponse.

$$P_{\rm ph,PV} = \gamma \frac{P_{\rm in}}{E_{\lambda}} \tag{1a}$$

and

$$N_{\rm ph,PV} = \gamma \frac{P_{\rm in}T}{E_{\lambda}} \tag{1b}$$

where *T* is the laser pulse width (200 ms in our case), P_{in} is the input optical power, and E_{λ} is the energy of a single photon of wavelength λ .

To relate the photoresponse to any changes in material properties, which shed light on the origins of the photoresponse due to electronic transition or ionic migration, we also measured the reflectivity spectrum of the device in areas subjective to voltage bias and light exposure using the HP70950A Optical Spectrum Analyzer (OSA). We used the calibrated, single-mode fiber-coupled white light source from the instrument as the incident light and measured the reflected light by the device. The reflected light was coupled to the same optical fiber and entered the optical spectrum analyzer via a 90/10 fiber-optic coupler.

Results. Because of the small (7 μ m diameter) active area of the device and the use of a GSG high-speed probe, we can characterize the device over a broad frequency range. Figure 3a shows the device frequency response from 5 Hz to 800 MHz at 4.5 μ W sinusoidally modulated optical input absorbed (639 nm wavelength). Due to instrumental limits, we have measured the frequency response using two instruments: a lock-in amplifier from ~5 Hz to 10 kHz and a vector analyzer and amplifier from 500 kHz to 800 MHz. It was apparent that the photoresponsivity was nearly independent of frequency within the measurement errors and gave rise to the value of around 10^{-3} A/W under 4.5 μ W. Additionally, Figure 3b shows the response of the perovskite photodetector to a 5 ns square pulse (~50 μ W) at a 639 nm wavelength.

To characterize the optical power dependence of the photoresponse, we also measured the power-dependent responsivity from 18 pW to 5 μ W under different frequencies (10 Hz, 0.5, 5, and 51 MHz). The log-log plot of responsivity is shown in Figure 4a. The log-log slopes are all close to -0.38 for 0.5, 5, and 51 MHz in the power range from 50 nW to 5 μ W. The log-log slope at 10 Hz also shows a similar slope of -0.41 for input power from 18 pW to 18 nW. Essentially these results show the power-dependent responsivity of $R \propto P^{-\beta}$ with $\beta \sim 0.4$ from 10 Hz to 51 MHz. From literature, we have found a similar relation was reported with $\beta \sim 0.5$. The value of β , which is typically between 0.4 and 0.5, is related to

the defect states density in perovskite, 17,18 and a detailed model between the defects and β will be presented separately.

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Next, we examined the responsivity under very low frequency (on the order of 0.1 Hz or quasi-persistent photoresponse). The slow response of photocurrent is obtained by taking the current difference before and after illumination by a single 200 ms optical pulse, as discussed in detail in the previous session on experimental setups and methods. The responsivity is obtained by dividing the photocurrent by the absorbed optical power by the perovskite layer. The log-log slope for slow-response responsivity under 639 nm is -0.89 between 14 aW and 6.9 fW (i.e., $R \propto P^{-\beta}$, $\beta \sim$ 0.9), as shown in Figure 4b. A similar correlation has also been reported in so-called DC measurements previously,^{15,16} showing that the internal responsivity as high as 10^7 A/W and its value decreases rapidly with increased power. Note that the main difference between our measurement and the conventional DC measurements is that the temporal response to a single optical pulse is directly measured, showing a very slow rise time of the device (in the order of 10 s).

We also observed the quasi-persistent photoresponsivity (i.e., the current does not return to the original dark current level without resetting the bias voltage (Figure 5). The good



Figure 5. Slow (quasi-persistent) response of the device to a single optical pulse containing a different number of photons. The orange line indicates the time when the optical pulse is applied. The black line is the measured dark current. The photocurrents (under excitations of a single photon and 440 photons) are obtained by subtracting the dark current from the total current.

stability of the dark current allows us to precisely measure the persistent photocurrent as small as 30 pA, which is well above the sensitivity limit (10 fA) of the instrument. By comparing Figure 4a,b, one interesting question arises: why the responsivity of a perovskite device shows two very different types of power dependence: one having a smaller slope of -0.4 and being frequency-independent (at least from 5 Hz to 800 MHz) and the other having a much steeper slope of -0.9 and

having a very slow rise time (around 20 s) and being quasipersistent. The most likely reason is that, in perovskite, there are two distinct physical mechanisms that give rise to the photoresponse. One mechanism is similar to a standard photodiode, where photon absorption generates electron—hole pairs traveling in opposite directions under bias, and such response is largely frequency-independent. On the other hand, the slow response is likely related to point defects and ion migration,^{19–22} which is slow but gives rise to the persistent photocurrent until the device is reset by moving the ions back to their original distribution.

What is most striking, however, is that we have found the slow (quasi-persistent) response can be further divided into two regimes: one showing the aforementioned relation (i.e., $R \propto P^{-\beta}$, $\beta \sim 0.9$) and another showing no power dependence (i.e., $R \propto P^{-\beta}$, $\beta \sim 0$). Due to the extremely low power level that distinguishes the two drastically different power-dependent relations, in the following, we use the number of photons absorbed by the device to discuss the two regimes.

In the slow (quasi-persistent) photoresponse regimes, tests were performed at both 518 and 635 nm with a similar range of power. The turning point for the power dependence of responsivity occurs at around 10 aW, where the responsivity reaches its maximum value of 1.7×10^7 A/W. At $\lambda = 518$ nm, a single photon of an energy of 2.39 eV (0.38 aJ) corresponds to a power level of 1.9 aW in a 200 ms optical pulse. The flat regime in Figure 6a corresponds to the response to 1–10



Figure 6. Quasi-persistent photoresponse (518 nm). (a) Average power-dependent photoresponse. (b) Statistical distribution of the photocurrent with the absorption of a single 518 nm wavelength photon. (c) Bias-dependent photoresponse to 8 photons of a 518 nm wavelength.

photons of the device. The full range of power in Figure 6a corresponds to 1–400 photons absorbed by the perovskite layer. When more than 10 photons are absorbed by the perovskite layer, the responsivity displays the relation of $R \propto P^{-\beta}$, $\beta \sim 0.9$.

A constant responsivity means that the output photocurrent of the perovskite detector is linearly proportional to the number of photons absorbed by the perovskite layer. Figure 6b shows the results of 40 measurements, with an average of 0.98 photons absorbed by the perovskite layer. It shows that by absorption of a single photon, the current is increased by around 30 pA on average. The quasi-persistent change in the material conductivity, revealed as persistent photocurrent, is most likely caused by redistributions of the ion and charged vacancy within the perovskite layer, which subsequently changes band bending and carrier injection efficiency at the ITO/perovskite junction.

Figure 6c shows the bias-dependent photoresponse with eight 518 nm wavelength photons absorbed. Below the bias of 0.62 V (corresponding to an average electric field of 1.55×10^4 V/cm in the 400 nm perovskite layer), the photoresponse drops rapidly.

For more supporting evidence of a macroscopic property change under optical excitation and external bias, we measured the reflectivity spectrum of the device before and after optical illumination under bias and after resetting the bias to 0 V. The observed reflective spectrum change indicates the change of composition distribution within the device due to this reversible process.^{23,24} Under white light illumination, the reflectivity peak of the device under bias shifted from 645 nm to around 630 nm, as shown in Figure 7a. After the light source and bias were turned off, the reflective peak shifted back after about 2 min, indicating that the perovskite layer returned to the original state by ion diffusion.²⁵ The observation with the



Figure 7. Reversibility of the internal amplification process. (a) Relative reflective spectrum. The brown circle line is reflectivity upon the device area before illumination; the orange star line is reflectivity after illumination with applied bias, and the navy triangle line is reflectivity 2 min after bias was turned off. (b) Band bending under bias due to the accumulation of changed ions after photon absorption. (c) Recovery with reversed bias and with diffusion in the dark. When $(I-I_{dark})/I_{dark} < 0.1$, the current difference is smaller than 10 pA, and the device is considered to reset.

quasi-persistent photoresponse behavior lead to the proposed potential band diagram change due to charged ion and vacancies accumulation near the electrodes, as illustrated in Figure 7b. We have studied two reset conditions: setting the bias to 0 V and reversing the bias from 1 V to -1 V. The first condition relies on iodide diffusion in the dark, and the second condition uses an opposite field to accelerate the motion of iodide. As shown in Figure 7c, under zero bias, the device needs 140 s to have its dark current return to its original value; while under the second condition, the device dark current is reset in 70 s.

The electrical conductivity change can be modeled by the distribution of charged oxygen vacancy V^+ 's and iodides within perovskite. By moving a given amount of iodides toward the anode and the same amount of V^+ to the cathode to maintain charge neutrality, we obtain the band bending of perovskite, and the current under bias can be calculated from the thermionic emission model in eq 2:

$$J_{\rm T} = AT^2 \exp\left(-\frac{q\varphi_{\rm B}}{kT}\right) \left(\exp\left(\frac{qV}{kT}\right) - 1\right)$$
(2)

where A = Richardson coefficient, T = 300 K, $\varphi_{\rm B}$ = Schottky barrier height, V = applied bias, q = electron charge, and k = Boltzmann constant. Taking the ratio between the total current (photocurrent plus dark current) and the dark current and using eq 2, we can obtain the change in Schottky barrier height $\Delta \varphi_{\rm B}$, in eq 3:

$$\frac{I_{\rm ph} + I_{\rm d}}{I_{\rm d}} = \exp\left[-\frac{q}{kT}\Delta\varphi_{\rm B}\right]$$
(3)

Using the relation $\Delta \varphi_{\rm B} = \varphi_{\rm B} - \varphi_{\rm B_o} = -\sqrt{qE/4\pi\varepsilon_0\varepsilon_{\rm r}}(E =$ electric field, ε_0 = permittivity of free space, $\varepsilon_{\rm r}$ = dielectric constant of perovskite), we can find the relation between the electric field at the perovskite/ITO interface and the measured currents, as shown in eq 4:

$$E = 4\pi\varepsilon_0\varepsilon_r \left[\ln\left(\frac{I_{\rm ph} + I_{\rm d}}{I_{\rm d}}\right) \frac{kT}{q^{3/2}} \right]^2$$
(4)

From Gauss law, $\varepsilon_0 \varepsilon_r (E - E_0) = q N_{\rm I}$, where $N_{\rm I}$ is the surface density $(\#/m^2)$ of accumulated iodides and V⁺'s near the ITO/ perovskite interfaces, and E_0 is the field in the charge-neutral region. When this relation was substituted into eq 4, we can find the number of iodides, $N_{\rm I}$. This brings up a very important observation: absorption of a single photon generates as many as $10^{8-9} \mbox{ for } I^- \mbox{ and } V^+ \mbox{ ion-vacancy pairs to move to their new }$ positions (i.e., from Figure 7a to Figure 7b). Up until now, all measurements of perovskite photodetectors have not kept track of the actual number of photons absorbed by perovskite, and all of the reported results to date have assumed that the absorption of each photon creates no more than one I^-/V^+ pair. By carefully keeping track of the actual number of photons absorbed by the perovskite layer and the number of I^-/V^+ pairs that are excited and redistributed, we have shown that the absorption of a single photon can lead the redistribution of 10^{8-9} for I^-/V^+ pairs. Furthermore, the results obtained in Figure 6c suggests the existence of the threshold electoral field of 1.55×10^4 V/cm for the motions of I^-/V^+ pairs. Below this critical field, single-photon absorption does not cause massive motions of I^-/V^+ pairs. Additionally, the characteristics in Figure 6a indicate that those movable $I^-/$

 V^{+} pairs would almost be depleted after the 7 μm diameter device absorbs 8–10 photons. In other words, the perovskite layer seems to contain a limited number of "excitable" I^{-}/V^{+} pairs. After all of these excitable I^{-}/V^{+} pairs are already migrated toward the anode and cathode, additional photon absorption has a small effect in material conductivity, thus showing the responsivity nearly inversely proportional to the input optical power.

These observations prompt us to suggest the existence of an avalanche-like process for the I^-/V^+ pairs in organometallic halide perovskites and ionic impact ionization process above the threshold field of 1.55×10^4 V/cm. Similar to electronic impact ionization where the kinetic energy of an electron can ionize an e—h⁺ pair in a cascade process^{26–29} or shallow trap assisted photomultiplication in an organic photodetector,^{30–32} perhaps a photoexcited I⁻ can gain sufficient energy from the applied field to ionize an I⁻ and V⁺ pair and trigger the cascade process.

On the other hand, the trap filling process^{33–35} could impede the proposed ionic impact ionization process in perovskite. When the bias level is low, the mobile iodide needs to travel a longer distance to gain enough energy to trigger another cycle of ionic impact ionization. A longer travel distance reduces the number of ionic impact ionization cycles as well as increases the probability of encountering a trap level, which decreases the photoresponse under lower bias. From Figure 6c, the photoresponse drops dramatically below 0.62 V due to the insufficient field of acceleration and the trap filling process. Regardless of the detailed physical mechanism, we have made the first observation that the energy of a single photon (~0.38 aJoule) can appreciably change the conductivity of perovskite, and such change is measurable, quasipersistent, and resettable.

Discussion and Conclusion. In a 7 μ m diameter perovskite photodetector, we investigated the frequency and optical power-dependent responsivity. We observed that the device showed two different power-dependent responsivities: one being similar to conventional photodetectors and the other being quasi-persistent and sensitive to very low optical power up to a single photon. By careful measurements of a photoresponse of the perovskite device down to the singlephoton level, we discovered that MAPbI₃ perovskite can change its macroscopic electric properties by absorbing the energy of a single photon (about 0.38 aJ). This phenomenon cannot be explained without an internal amplification mechanism that can cause the collective motion of a massive number of iodide by absorption of only a few photons.

The main contribution of our work is to report the first observation that macroscopic electric and optoelectronic properties of perovskite thin films can be altered or programmed by a few photons or even a single photon carrying extremely low (aJoule) energy. The detailed physical mechanism that gives the device its extremely high sensitivity and persistent response requires further experimental and theoretical investigations. One particularly promising application utilizing this internal amplification process is an analogue memory device for neuromorphic computing.36,37 The lowenergy operation triggered by even single-photon irradiation provides large benefits in the computing system. The cascadic behavior allows us to develop new types of multistate memory with the forming-free property and new logic circuit architecture. Since the slow response can come from collective ionic motions, some electronic device applications such as a high-speed transistor may be limited, but many new device applications, including energy harvesting, high capacity memory, and optical switches, are expected. For example, the development of photo/electrochromic devices with a low power operation and high response speed is expected. The simple device structure and solution process are ideal for lowcost, highly integrated practical applications and mass production. Although there are several technological challenges, including stability issues of this material group, novel cascadic ion migration behavior as well as the other high-speed operation regime gives us ample opportunities to create new device applications based on hybrid perovskites. We anticipate our work will create new avenues for research and applications of the perovskite device and material.

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Author Contributions

 $^{\perp}$ Z.X. and Y.Y. initiated the project and contributed equally to the project. Z.X. and Y.Y. led device fabrication, and S.A. and

J.Z. participated in the device fabrication. Y.C. and Y.L. assisted the perovskite spin-coating. Y.Y. took the lead for highsensitivity device characterization, and Z.X. took the lead for high-frequency response characterization. Y.Y., Z.X., and S.A. were all involved in device characterization. Y.Y and S.A performed reflectivity measurement and analysis. I.A.N. performed Matlab simulation. Z.X wrote the Labview Programs. K.N. consulted the device modeling, S.X. consulted the perovskite fabrication, and Y.H.L. started and oversaw the entire project. Z.X., Y.Y., S.A., I.A.N., M.A.R.M., A.Z., Y.Z., L.Y., K.N., S.X., and Y.H.L. were involved in device design and mechanism discussion. Z.X. and Y.Y. carried out data analysis and wrote the manuscript. All authors discussed the results and commented on the manuscript. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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